Notes

(*p*-cymene)RuLCl$_2$ (L = 1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene and 1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene) and Related Complexes as Ring Closing Metathesis Catalysts

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Summary: Complexes of (η^6-arene)ruthenium bearing the carbene ligand 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) and 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene (IPr) Ru(IMes)(Cl)$_2$(η^6-arene), Ru-(IPr)(Cl)$_2$(η^6-arene), and [Ru=C=C=CPh$_2$(IMes)(Cl)(η^6-arene)]PF$_6$ were prepared and found to be efficient catalyst precursors for ring closing olefin metathesis.

Introduction

Recent developments in the area of olefin metathesis have had a tremendous impact on this field.[1] The use of the ruthenium carbene complex, RuCl$_2$(=C(H)Ph)-(PCy$_3$)$_2$ (**1**), developed by Grubbs et al. in organic and polymer chemistry is now widespread.[1a,b,2] Although **1** is a highly efficient and tolerant catalyst precursor for numerous metathetical reactions,[3] recently, alternative metathesis catalyst precursors that are more accessible and have comparable activity have been introduced.[4] For example, it has been shown that (*p*-cymene)RuCl$_2$-(PCy$_3$) (**2**), and its cationic, 18-electron allenylidene derivative, [(*p*-cymene)RuCl(PCy$_3$)(=C=C=CPh$_2$)]PF$_6$ (**3**), are active catalyst precursors for various ring closing metathesis (RCM) reactions.[4a,b,5] In every example mentioned above the use of sterically demanding and electron-donating phosphines is required to stabilize reactive intermediates. We have previously shown that the nucleophilic carbene ligand, 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) (**4**), can act as a tertiary phosphine analogue and is capable of supporting metathesis activity.[6] The increased catalytic activity in ring closing metathesis reactions was illustrated in the case of the IMes analogue of the Grubbs' catalyst, RuCl$_2$(=C(H)Ph)(PCy$_3$)(IMes) (**5**). The role of the IMes ligand is twofold: IMes is a better donor than PCy$_3$ and it is more sterically demanding, which helps prevent (or slow) bimolecular carbene decomposition. Recently, we have been able to synthesize 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) (**6**). To study the effect of replacing a phosphine donor with the IMes or IPr ligand, we now describe the synthesis and characterization of (*p*-cymene)RuCl$_2$(IMes) (**7**), (*p*-cymene)RuCl$_2$(IPr) (**8**), and [(*p*-cymene)RuCl(IMes)(=C=C=CPh$_2$)]PF$_6$ (**9**). Furthermore, the catalytic activities of **7**, **8,** and **9** in RCM reactions has been investigated and are compared to those of the phosphine-containing complexes (*p*-cymene)RuCl$_2$(PCy$_3$) (**2**) and (*p*-cymene)RuCl$_2$(P*i*-Pr$_3$) (**10**).

Results and Discussion

Reaction of the commercially available [(*p*-cymene)-RuCl$_2$]$_2$ (**11**) with IMes or IPr in THF at room temperature resulted in the formation of orange microcrystalline solid (*p*-cymene)RuCl$_2$(IMes) (**7**) and brown microcrystalline solid (*p*-cymene)RuCl$_2$(IPr) (**8**) in 90% yields, respectively. Complexes were characterized by ^{1}H NMR spectroscopy and elemental analysis (see Experimental Section). When **7** is reacted with 1,1-diphenylprop-2-ynyl alcohol in the presence of NaPF$_6$, [(*p*-cymene)RuCl-

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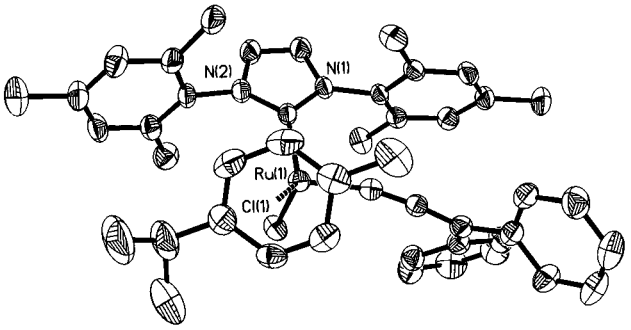
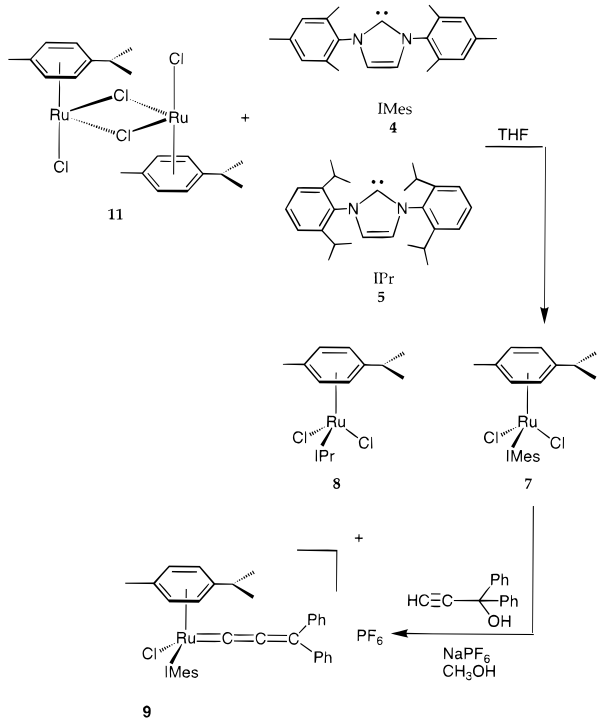


Figure 1. ORTEP of (*p*-cymene)RuCl(IMes)(=C=C=CPh$_2$)-PF$_6$ (**9**) with ellipsoids drawn with 50% probability. Hydrogen atoms and PF$_6$ counterion have been omitted for clarity.

Scheme 1



(IMes)(=C=C=CPh$_2$)]PF$_6$ (**9**) is produced as brown crystals in 91% yield (Scheme 1).

Complex **9** is characterized by ^{1}H NMR spectroscopy and elemental analysis. The X-ray crystal structure of **9** has been determined, and an ORTEP of **9** is shown in Figure 1. The coordination geometry around the Ru center can be considered a three-legged piano stool. *p*-Cymene is bound to ruthenium in a η^6 fashion; the isopropyl groups on the arene are distorted away from the metal center presumably due to unfavorable steric factors. The two mesityl groups on the IMes ligand are bent toward the ruthenium center with the dihedral angles of 78.2(2)° and 89.9(2)°, providing steric crowding, which appears beneficial in RCM reactions.[2c,6] The allenylidene group is not linear but rather bent at the middle carbon (C22−C23−C24 = 171.8°). The Ru−C22 (1.890(4) Å) bond distance is considerably shorter than the Ru−C10 single bond (2.077(4) Å). Selected bond lengths and bond angles are reported in Table 2.

The catalytic activities of **7**, **8,** and **9** have been tested by using the standard ring closing metathesis (RCM) substrate, diethyldiallylmalonate (eq 1), and compared to those of (*p*-cymene)RuCl$_2$(PR$_3$) (R = Cy (**2**) and *i*-Pr (**10**)). Results are presented in Table 3.

Table 1. Crystallographic Data for Complex 9

formula	$C_{53.56}H_{61.25}ClF_6N_2O_2PRu$
fw	1046.54
color	brown
space group	*P*2(1)/*c*
a, Å	18.8203(7)
b, Å	17.4709(6)
c, Å	15.9621(6)
α, deg	90
β, deg	104.5250(10)
γ, deg	90
volume (Å^3), *Z*	5080.7(3), 4
density (calcd) (g/cm^3)	1.368
R	0.0479
R_w	0.1313
no. refined params	754
no. data collected	57962
no. unique data, $I > 3\sigma$	8945
goodness of fit, F^2	0.941

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 9

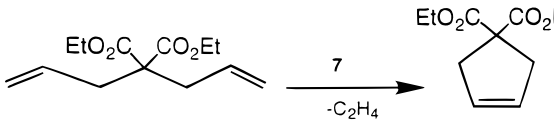
Ru(1)−C(22)	1.890(4)	C(22)−Ru(1)−Cl(1)	84.95(12)
Ru(1)−C(10)	2.077(4)	C(22)−Ru(1)−C(10)	92.62(15)
Ru(1)−C(39)	2.224(5)	C(10)−Ru(1)−Cl(1)	85.38(11)
Ru(1)−C(40)	2.249(4)	C(22)−C(23)−C(24)	171.8(4)
Ru(1)−C(38)	2.356(4)	Ct−Ru−C(34)	131.8
Ru(1)−C(37)	2.383(4)	Ct−Ru−C(59)	122.9
Ru(1)−Ct*[a]	1.804(4)	Ct*−Ru−Cl(1)	125.4
Ru(1)−Cl(1)	2.3903(11)		
Ru(1)−C(42)	2.246(4)		
Ru(1)−C(41)	2.258(4)		

[a] *Ct is the center of the arene ring.

Table 3. Ring Closing Metathesis of Diallylmalonate Using Catalyst Precursors 2, 7, 8, 9, and 10

entry	catalyst precursor	solvent	temp (°C)	time (h)	conversion (%)[b]
1	**2**	CD_2Cl_2	40	27	47
2	**10**	CD_2Cl_2	40	27	48
3	**9**	CD_2Cl_2	40	27	85
4	**7**	CD_2Cl_2	40	27	78
5	**8**	CD_2Cl_2	40	27	40
6	**8**[a]	CD_2Cl_2	40	27	40
7	**7**	toluene-d_8	80	2	100
8	**7**[a]	toluene-d_8	80	2	100
9	**8**	toluene-d_8	80	2	100

[a] The experiment was performed in the absence of light. [b] Calculated from NMR spectra.



(1)

When the reactions were carried out in CD_2Cl_2 and heated to 40 °C, **9** catalyzed reaction 1 with a conversion of 85%, whereas **7** showed a conversion of 78%. The use of **2** and **10** as catalyst precursors led to the yields of 48% and 47%, respectively, after 27 h (Table 3, entries 1−4). The catalytic activity of **8** at this temperature (40% yield, Table 3, entry 5) was in the range of those of the phosphine-containing complexes **2** and **10**. To investigate the role of solvent, temperature, and light, RCM was performed with **7** and **8** as the catalyst precursors and toluene-d_8 as the solvent. Upon heating the reaction mixtures to 80 °C, a 100% conversion to

product was observed after only 2 h in both cases (Table 3, entries 7−9). Performing the reactions in the dark did not change the outcome and yields of the reactions (Table 3, entries 6 and 8), which would indicate that the catalytic reactions are not photoinduced. This is in contrast with the complexes of the type M(*p*-cymene)-$Cl_2(PR_3)$ (M = Ru, Os; R = Cy, *i*-Pr), which have been reported to become active ROMP catalysts only when activated by UV irradiation.[7] It has also been reported that RCM in the presence of [(*p*-cymene)(PCy_3)ClRu=C=C=CPh_2]PF_6 and Ru(*p*-cymene)$Cl_2(PCy_3)$ is accelerated by exposure to UV or neon light.[4b,5b] No such effect is observed for our system. Examination of data gathered in Table 3 shows that the IMes-containing complexes **7** and **9** are the best catalyst precursors found in this study, whereas the ruthenium complex incorporating the IPr ligand, **8**, showed similar reactivity to those of **2** and **10**. Solution calorimetric investigations indicate that the Ru−L bond strength decreases in the following order: Ru−IMes (15.6 kcal/mol) > Ru−IPr (11.2 kcal/mol) > Ru−PCy_3 (10.5 kcal/mol) > Ru−P*i*-Pr_3 (9.4 kcal/mol).[6a,8] The IMes ligand proved to be a stronger binder than the IPr ligand, whose relative enthalpy is comparable to that of the PCy_3 ligand. The initial step in the ring closing metathesis mechanism using the (*p*-cymene)$RuLCl_2$ complexes must involve the formation of a ruthenium−carbene complex,[2c,9] and in the case of ruthenium−arene complexes the carbene moiety can presumably be formed by the change in the hapticity of the arene ring, leading to vacant sites on Ru. The more electron-donating ligand (IMes) can facilitate this process more easily than either IPr or the phosphines, and this reason is proved to be the origin of the higher catalytic activity of **7** compared to those of **8**, **2**, and **10** at 40 °C. When the temperature is raised to 80 °C, both **7** and **8** show the same activity. It could be argued that at higher temperatures the activation barrier for the change in arene hapticity has already been overcome and under these conditions the electronic differences between the ligands are not very important.

We have shown that the ruthenium complexes incorporating the nucleophilic carbene ligands 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) (**4**) and 1.3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) (**6**) are more active catalyst precursors in RCM reactions than those containing phosphine ligands. These RCM reactions are not light induced and proceed to completion at higher temperatures (27 h at 40 °C vs 2 h at 80 °C). The novel complexes display high stability at elevated temperatures.

Experimental Section

General Considerations. All manipulations involving organoruthenium complexes were performed under inert atmospheres of argon or nitrogen using standard high-vacuum or Schlenk tube techniques or in an M Braun glovebox containing less than 1 ppm oxygen and water.

Starting Materials. The phosphine ligands, 1,1-diphenyl-prop-2-ynyl alcohol and diethyl allyllmalonate, were purchased from Strem Chemicals, Aldrich, or Organometallics, Inc., and were used as received. Methylene chloride was distilled from CaH_2, and toluene was dried over Na/K and vacuum transferred to flame-dried glassware. NMR spectra were recorded using a Oxford 400 MHz spectrometer.

The compound [$RuCl_2$(*p*-cymene)]$_2$ (**11**)[10] and carbene ligands 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) (**4**)[11] and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) (**6**)[8] were synthesized according to the literature procedure. The synthesis of other organoruthenium complexes, (*p*-cymene)-$RuCl_2$(P(*i*-Pr)$_3$) (**10**) and (*p*-cymene)$RuCl_2(PCy_3)$ (**2**), have previously been reported.[12] Experimental synthetic procedures, leading to isolation of previously unreported complexes, are described below.

General Procedure for Synthesis of (*p*-cymene)$RuCl_2$-(IMes) (7) and (*p*-cymene)$RuCl_2$(IPr) (8). A 100 mL flask was charged with 0.970 g (1.58 mmol) of [$RuCl_2$(*p*-cymene)]$_2$, 3.186 mmol of IMes (**4**) or IPr (**5**), and 30 mL of THF. The clear orange solution was stirred at room temperature for 60 min, after which the solvent was removed under vacuum. The residue was washed with hexane (2 × 10 mL), filtered, and dried under vacuum, which afforded the tan product (yield: 90%).

For (7): ^{1}H NMR (400 MHz, THF-d_8) δ 1.08 (d, J = 7.2 Hz, 6H, CH(CH_3)$_2$), 1.51 (s, 3H, CH_3), 2.22 (s, 12H, Mes-2,6-CH_3), 2.32 (s, 6H, Mes-4-CH_3), 2.43 (m, 1H, CH(CH_3)$_2$), 4.55 (d, J = 6 Hz, 2H, C$_6H_4$), 5.00 (d, J = 6 Hz, 2H, C$_6H_4$), 6.90 (d, 4H, Mes-3, 5-*H*), 7.05 (s, 2H, NC*H*C*H*N). Calcd for $C_{31}H_{38}N_2Cl_2Ru$: C, 60.98; H, 6.27; N, 4.59. Found: C, 60.64; H, 6.20; N, 4.31.

For (8): ^{1}H NMR (400 MHz, C_6D_6) δ 1.00 (d, J = 6.4 Hz, 12H, IPr CH(CH_3)$_2$), 1.05 (d, J = 7.0 Hz, 3H, *p*-cymene CH-(CH_3)$_2$), 1.15 (d, J = 7.0 Hz, 3H, *p*-cymene CH(CH_3)$_2$), 1.46 (d, J = 6.4 Hz, 12H, IPr CH(CH_3)$_2$), 1.75 (s, 3H, *p*-cymene CH_3), 2.72 (m, 1H, *p*-cymene CH(CH$_3$)$_2$), 3.24 (m, 4H, IPr CH(CH$_3$)$_2$), 4.48 (d, J = 6 Hz, 2H, *p*-cymene C$_6H_4$), 4.85 (d, J = 6 Hz, 2H, *p*-cymene C$_6H_4$), 6.47 (s, 2H, NC*H*C*H*N), 7.03 (t, J = 7 Hz, 1H, IPr C$_6H_4$), 7.10 (d, J = 9 Hz, 4H, IPr C$_6H_4$), 7.22 (t, J = 7 Hz, 1H, IPr C$_6H_4$). Calcd for $C_{37}H_{50}N_2Cl_2Ru$: C, 63.96; H, 7.25; N, 4.03. Found: C, 64.20; H, 7.30; N, 4.10.

(*p*-cymene)RuCl(IMes)(=C=C=CPh_2)PF_6 (9). A 50 mL flask was charged with 118 mg (0.568 mmol) of 1,1-diphenyl-prop-2-ynyl alcohol, 231.2 mg (0.3786 mmol) of (*p*-cymene)-$RuCl_2$(IMes), 200 mg (760 mmol) of $NaPF_6$, and 20 mL of MeOH. The reaction mixture was stirred at room temperature overnight. The solvent was then evaporated in vacuo, and the residue was extracted with CH_2Cl_2 (20 mL). Filtration and removal of the volatiles yielded a brown solid, which was washed with hexanes (2 × 5 mL) and then dried under vacuum to afford 467 mg of the red-brown product (yield: 91%). The crude product can be purified by recrystalization from CH_2-Cl_2−hexane to obtain the dark brown crystals: ^{1}H NMR (400 MHz, THF-d_8) δ 1.08, 1.17 (d, J = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.99 (s, 3 H, CH_3), 2.04, 2.15, 2.18, 2.53 (s, 18 H, Mes-2, 4, 6-CH_3), 3.22 (m, 1H, CH(CH$_3$)$_2$), 5.17, 5.54, 5.68, 5.85 (d, 4 H, C$_6H_4$, J = 6 Hz), 7.12−7.86 (m, 16 H, all the other Ar−*H* and NC*H*C*H*N). Calcd. for $C_{31}H_{38}N_2Cl_2Ru$: C, 60.69; H, 5.31; N, 3.08. Found: C, 60.64; H, 5.21; N, 3.31.

Ring Closing Metathesis Procedure. In the drybox catalyst precursor (5 mol %) was accurately weighed in a Wiland screw-capped NMR tube and dissolved in CD_2Cl_2 or toluene-d_8 (0.4 mL). Diethyldiallyl malonate (0.02 g, 0.1 mmol) was added to the solution, and the sealed NMR tube was heated to 40 °C in the case of CD_2Cl_2 and to 80 °C when

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toluene-d_8 was used as the solvent. Product formation and diene disappearance were monitored by integrating the allylic methylene peaks. Product formation was confirmed by comparison with literature NMR data.[9] The reactions were carried out under an ordinary neon lamp. For the reactions that were performed in the absence of light, the NMR tubes were wrapped in aluminum foil.

X-ray Diffraction Measurements. A single crystal of **9** was coated with paratone oil and then sealed in a glass capillary tube. The X-ray data were collected at low temperature using graphite-monochromated Mo Kα radiation on a Siemens P4 automated X-ray diffractometer. The structure was solved using direct methods (SHELXS-86) and refined by full matrix least-squares techniques. Initial fractional coordinates for the Ru atom were determined by heavy-atom methods, and the remaining non-hydrogen atoms were located by successive difference Fourier calculations, which were performed with algorithms provided by SHELXTL IRIS operating on a Silicon Graphics IRIS Indigo workstation. Crystallographic data can be found in Table 1, and selected bond distances and bond angles are presented in Table 2.

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Supporting Information Available: Details of crystal structure determinations for **9** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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